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Theory of thermodynamic fluctuations

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The paper is on a statistical theory of thermodynamic fluctuations based on Kullback's measure of directed divergence.

1. Introduction

The theory of macroscopic fluctuations both for equilibrium and non-equilibrium phenomena plays a significant part in statistical physics. There are different approaches to the problems of thermodynamic fluctuations of a system in equilibrium e.g., Gibbs' thermodynamical method, the method of Einstein's fluctuation probability etc. A generalization of the thermodynamic fluctuation theory is due to Greene & Callen (1951). In this paper we have studied the problem of fluctuations by taking suitable statistical model of thermodynamic system. The theory, we have presented, is based on some general results of mathematical statistics and information theory. Here we have also made extensions and corrections of a few results of an earlier paper (Chakrabarti 1970).

2. Thermodynamic Description of the System

We consider a large thermodynamic system. The macroscopic description of the system is characterized by a small number of variables. These variables may be the extensive properties (such as the energies, masses, electric charges etc.) of macroscopic infinitesimal sub-regions within the system. The regions should on microscopic scale contain a large number of particles so that the principle of statistical mechanics may be applied to them (Mazur 1961). We shall assume such extensive variables to be additive.

Now let the equilibrium state of any sub-region be characterized by the set of extensive variables x_α and the intensive variables θ_α $(\alpha = 1, 2, \ldots, n)$. These intensive variables are the temperature, chemical potential, pressure etc. Let $f(x, \theta)$ be the equilibrium distribution of x_α $(\alpha = 1, 2, \ldots, n)$. For the development of a statistical theory we consider our system as an assembly of N similar sub-regions where N is large enough so that the system under consideration be really a thermodynamic one. The distribution for the assembly is given by

$$P(x, \theta) = P(x_1, x_2, \ldots, x_n; \theta_1, \theta_2, \ldots, \theta_n) = \prod_{i=1}^{N} f(x^i, \theta), \tag{1}$$

where

$$x = (x_1, x_2, \ldots, x_n), \qquad x_\alpha = \sum_{i=1} x_\alpha{}^i,$$

$$x^i = (x_1{}^i, x_2{}^i, \ldots, x_n{}^i), \qquad \theta = (\theta_1, \theta_2, \ldots, \theta_n).$$

3. Deviation from Equilibrium

Let us now consider a deviation of the system from equilibrium to a neighbouring non-equilibrium state. The usual method of obtaining such a transition consists in the deviation of the extensive variables. Instead we shall adopt the local intensive variables θ_α as the fluctuating parameters (Prigogine 1961). Let $\Delta\theta_\alpha$ be the deviations of θ_α from their equilibrium values. Let $P(x, \theta+\Delta\theta)$ be the new distribution corresponding to the parametric values $\theta+\Delta\theta$ and since $\Delta\theta_\alpha$ are small, we assume that $P(x, \theta+\Delta\theta)$ preserves its functional form.

We shall now introduce a measure of divergence (or distance) Δs between the two probability distributions $P(x, \theta)$ and $P(x, \theta+\Delta\theta)$ as (Kullback 1959)

$$\Delta s^2 = 2K(\theta+\Delta\theta, \theta) \qquad \ldots \quad (2)$$

where

$$K(\theta+\Delta\theta, \theta) = \int P(x, \theta+\Delta\theta) \log \frac{P(x, \theta+\Delta\theta)}{P(x, \theta)} dx$$

is known as Kullback's information or gain of information (Rényi 1969) and is related to the entropy produced within the system for transition from the neighbouring non-equilibrium state to the equilibrium state (Schlögl 1966). If the deviation from equilibrium is small, neglecting higher order terms of $\Delta\theta_\alpha$, we have

$$\Delta s^2 = 2K(\theta+\Delta\theta, \theta) = \sum_{\alpha\beta} H_{\alpha\beta}\Delta\theta_\alpha\Delta\theta_\beta, \qquad \ldots \quad (3)$$

where

$$H_{\alpha\beta} = \left\langle \frac{\partial^2}{\partial\theta_\alpha\partial\theta_\beta} \log P \right\rangle = N\left\langle \frac{\partial^2}{\partial\theta_\alpha\partial\theta_\beta} \log f \right\rangle = NB^2{}_{\alpha\beta}$$

are the elements of Fisher's information matrix (Kullback 1959).

4. Thermodynamic Equilibrium and Fluctuations

For thermodynamic equilibrium the distance Δs given by (3) should be minimum for given averages $< x_\alpha >$ and $\Delta\theta_\alpha$. The lower bound of Δs^2 is provided by the information-inequality of Cramer-Rao (Kullback 1959). The minimum value of

$$\sum_{\alpha,\beta} H_{\alpha\beta}\Delta\theta_\alpha\Delta\theta_\beta \quad \text{is} \quad \sum_{\alpha,\beta} \frac{\partial < x_\alpha >}{\partial\theta_\beta} \qquad \frac{\partial < x_\beta >}{\partial\theta_\alpha} \Delta\theta_\alpha\Delta\theta_\beta,$$

where $L_{\alpha\beta} = <\Delta x_\alpha.\Delta x_\beta>$ is the co-variance of x_α and x_β and in that case $P(x, \theta)$, in particular, is given by (Kullback 1959)

$$P(x, \theta) = \exp\,(\sum_\alpha \theta_\alpha x_\alpha) h(x_1, x_2, \ldots, x_n)/Z(\theta_1, \theta_2, \ldots, \theta_n) \qquad \ldots \quad (4)$$

where

$$<x_\alpha> = \frac{\partial}{\partial\theta_\alpha} \log Z(\theta_1, \theta_2, \ldots, \theta_n). \qquad \ldots \quad (5)$$

The distribution (4) is the generalized canonical distribution of x_α $(\alpha = 1, 2, \ldots, n)$ and eqs. (5) are identical with the maximum-likelihood equations (Wilks 1962)

$$\left\langle \frac{\partial}{\partial\theta_\alpha} \log P \right\rangle = 0, \qquad \ldots \quad (6)$$

so that the equilibrium parameters θ_α determined by the eqs. (5) are nothing but the maximum-likelihood estimates (Wilks 1962). This property is very important for further development.

For thermodynamic equilibrium we have then

$$H_{\alpha\beta} = \frac{\partial <x_\alpha>}{\partial\theta_\beta} \; L_{\alpha\beta}{}^{-1} \frac{\partial <x_\beta>}{\partial\theta_\alpha}.$$

But from (4) and (5)

$$H_{\alpha\beta} = \left\langle \frac{\partial^2 \log D}{\partial\theta_\alpha \partial\theta_\beta} \right\rangle = \frac{\partial <x_\alpha>}{\partial\theta_\beta} = \frac{\partial <x_\beta>}{\partial\theta_\alpha}$$

So that

$$L_{\alpha\beta} = <\Delta x_\alpha.\Delta x_\beta> = \frac{\partial <x_\alpha>}{\partial\theta_\beta} = \frac{\partial <x_\beta>}{\partial\theta_\alpha}. \qquad \ldots \quad (7)$$

The above is the *Fluctuation-dissipation* theorem of equilibrium thermodynamics, the right hand members $\partial <x_\alpha>/\partial\theta_\beta$ or $\partial <x_\beta>/\partial\theta_\alpha$ are generalized susceptibilities. If we put $\alpha = \beta$, we get the expressions for the fluctuations of the extensive variables

$$<(\Delta x_\alpha)^2> = \frac{\partial <x_\alpha>}{\partial\theta} = \frac{\partial^2}{\partial\theta_\alpha^2} \log Z \qquad \ldots \quad (8)$$

which is an extension of Khinchin's result (Khinchin 1949).

5. Fluctuation—Probability

The distance Δs given by $\Delta s^2 = N \sum_{\alpha\beta} B^2{}_{\alpha\beta} \Delta\theta_\alpha \Delta\theta_\beta$ is normal (N (0, 1) for large N (Wilks 1962). We can then define the fluctuation probability by

$$\text{Prob}\,(\Delta s) = \omega \sim e^{-\frac{1}{2}\Delta s^2}$$

or

$$\omega \propto e^{-\overline{K}(\theta+\Delta\theta,\theta)} \qquad \ldots \quad (9)$$

which is similar to the form derived by Schlögl (1968). Alternatively this can be expressed as (Chakravarti 1974)

$$\omega \,\alpha\, \exp\left(\frac{\partial^2 S}{zk}\right) \qquad \dots \quad (10)$$

where

$$S = -k \left\langle \log \frac{P(x, \theta)}{h(x_1, \dots x_n)} \right\rangle,$$

is the entropy of the system. The formula (10) is valid for a generalized thermodynamic system near thermodynamic equlibrium.

6. Fluctuations: Intensive Parameters

We have seen that the parameters θ_α corresponding to the equilibrium state are the maximum-likelihood estimates. For large N, θ_α has a distribution which is asymptotically normal $N(\theta_\alpha, \| NB_{\alpha\beta} \|^{-1})$ so that for large N

$$<(\Delta\theta_\alpha)^2> = 1/NB_{\alpha\alpha}{}^2 = 1/\left\langle \left(\frac{\partial \log P}{\partial \theta_\alpha}\right)^2 \right\rangle.$$

Thus for a thermodynamic system the fluctuations of intensive variables are given by

$$<(\Delta\theta_\alpha)^2> = 1/<(\Delta x_\alpha)^2>,$$

where x_α is the extensive variable conjugate to θ_α.

As an example, let us consider the fluctuation of temperature of the system assuming that all the extensive variables other than the energy are fixed. This is given by

$$<(\Delta\theta)^2> = 1/<(\Delta E)^2> \qquad \dots \quad (11)$$

where E is the energy of the system.

On writing $\theta = 1/kT$, k is the Boltzmann's constant, T is the absolute temperature, we have

$$<(\Delta T)^2> = \left(\frac{dT}{\partial\theta}\right)^2 <(\Delta\theta)^2> = \frac{k^2T^4}{<(\Delta E)^2>} = \frac{kT^2}{C_v}, \qquad \dots \quad (12)$$

where C_v is the specific heat at constant volume. The above result agrees with that given by Landau & Lifshitz (1958).

7. Conclusions

(i) In determining the fluctuation of θ_α by eq. (11) we have assumed that all the extensive variables other than x_α remain fixed. A general result follows when x_α ($\alpha = 1, 2, \ldots, n$), are correlated and such a general formula can be obtained from the generalized fluctuation probability formula (10). In some earlier papers (Chakravarti 1971, 1974) we have discussed such a problem which possesses interesting physical significance.

(ii) Unlike the usual process of deviating the extensive variables from their equilibrium values, the present method consists in the deviations of the intensive variables to have a neighbouring non-equilibrium state. From physical point of view it is important. For, certain important thermodynamic measurements are made on intensive parameters. For example, it is temperature and not the dynamical variable like local energy that is measured and it is easier to treat these parameters (intensive) meaningfully with a canonical like distribution.

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